

# PATENT SPECIFICATION

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 (72) Inventor APPARAO TATYARAO LENGADE



## (54) HYDROCARBON CONVERSION CATALYSTS AND THEIR PRODUCTION

- (71) We, W. R. GRACE & CO., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7 Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the preparation of catalysts, more specifically of an improved highly attrition-resistant hydrocarbon conversion catalyst promoted with a crystalline aluminosilicate molecular sieve. (For the sake of brevity the term "zeolite" will hereinafter be used to denote aluminosilicate molecular sieves).
- It is generally known that zeolites having uniform pore dimensions of about 6—15 Å are extremely active hydrocarbon conversion catalysts. These zeolites, when converted to a stable low sodium form and combined with an appropriate inorganic oxide matrix, possess catalytic activity and selectivity characteristics which render them particularly useful in commercial catalytic cracking operations.
- A successful commercial catalyst must possess, in addition to the desired activity and selectivity, sufficient thermal stability and physical toughness and attrition-resistance to withstand the rigorous conditions which exist in commercial catalytic conversion units. Accordingly, to produce a successful commercial zeolite-promoted catalyst, particular care must be taken to select an appropriate matrix system which in addition to exhibiting the required physical and catalytic properties must be relatively inexpensive and readily available.
- Naturally occurring clays, such as kaolin, have been heretofore included in many cracking catalyst compositions. However, clays in general, while being cheap and readily available, are found to impart low strength and low resistance to attrition to many commercial cracking catalyst compositions.
- To date, relatively few commercial cracking catalysts which contain substantial amounts of clay possess the toughness and attrition-resistance exhibited by totally synthetic catalyst compositions.
- It is therefore an object of the present invention to provide an improved zeolite-promoted clay-containing hydrocarbon-treating catalyst which is exceptionally resistant to attrition.
- It has now been found that a mechanically strong, attrition-resistant clay-containing zeolite-promoted catalyst may be prepared by shaping a mixture containing at least finely-divided zeolite (as defined above), clay, an alumina sol as more particularly defined below and, optionally, also artificial amorphous silica or artificial amorphous alumina or an artificial amorphous silica-alumina composite, and drying and calcining the shaped composition. The mixture may be shaped by extrusion or pelletised to form a bead type catalyst for moving bed or fixed bed operation, or alternatively it may be spray dried to form microspheres for use in fluidised bed catalytic conversion units.
- The zeolite used in the preparation of the catalyst will generally comprise one or more synthetic crystalline aluminosilicates, such as a faujasite, which possess a uniform pore dimension of 6 to 15 Å. The zeolites particularly preferred are synthetic faujasites which possess a thermal stability of about 1500 to 1700° F. (i.e. are thermally stable up to such temperatures), a silica: alumina molar ratio of between 2.5 and 6.0 and a sodium content (calculated as Na<sub>2</sub>O) of less than 1%, preferably less than 0.5%. Zeolites which have been ion-exchanged with non-alkali metal cations, for example rare earth metal cations, and which have been stabilised by an intermediate heat treatment, are generally found to possess the catalytic activity and stability required. (All per-

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tages and "parts" are by weight except when otherwise stated).

The matrix component may comprise naturally occurring kaolin or halloysite clay, either in its native state or thermally or chemically modified, if desired in admixture with another clay. For example a mixture of Avery clay and kaolin may be used with good results. In general, these clays will possess a particle size of 0.1 to 10 microns and a surface area of 5 to 65 square metres per gram.

In addition to clay, the matrix may contain artificial amorphous silica or artificial amorphous alumina or, preferably, an artificial amorphous silica-alumina composite. A typical artificial amorphous silica-alumina composite will contain from 10 to 30% alumina and may be prepared by the gelation of sodium silicate with an inorganic acid or carbon dioxide followed by the addition of a suitable aluminium salt, for example aluminium sulphate, to provide the desired alumina content. The silica-alumina composite preferably comprises particles ranging in size from 10 to 110 microns and having a surface area of from 150 to 500 square metres per gram.

The alumina sol binder comprises aluminium hydroxide and aluminium trichloride in a  $\text{Al}(\text{OH})_3:\text{AlCl}_3$  molar ratio of between 4.5 and 7.0. It is preferably prepared by reacting aluminium metal with an aqueous solution of hydrochloric acid to form aluminium trichloride, according to the general reaction  $2\text{Al} + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2$ . The aluminium chloride formed subsequently reacts with water to yield a mixture of aluminium hydroxide and aluminium chloride in a molar ratio within the above range. In a particularly preferred method, the aluminium is reached with the aqueous hydrochloric acid at a temperature of 175 to 220° F. for 6–24 hours. The aqueous hydrochloric acid preferably contains from 0.5 to 1.5 moles HCl per litre and is used in an amount to provide preferably from 0.35 to 0.54 moles of HCl for each gram atom of alumina. The reaction yields an alumina sol which is a colourless to slightly bluish liquid and which is readily miscible with further water. Before use it will generally be diluted with water until its content of alumina (calculated as  $\text{Al}_2\text{O}_3$ ) is 15 to 30%, preferably 20 to 30%.

Suitable proportions for the several ingredients, per 100 parts of the mixture, are:

- 55 5 to 20 parts of zeolite (on a dry solids basis)
- 50 to 80 parts clay
- 0 to 30 parts synthetic amorphous matrix component
- 5 to 15 parts alumina sol (calculated as  $\text{Al}_2\text{O}_3$  on a dry solids basis).
- 60

A general procedure for preparing the catalysts includes mixing the zeolite component with the clay component to give a dry mixture

and subsequently adding the alumina sol having the desired  $\text{Al}_2\text{O}_3$  content. The product is then mixed to a plastic consistency, which requires about 20 minutes mixing time. This plastic mixture may then be formed into pellets by extrusion through an appropriate die, e.g. of diameter from 3/16 to 3/8 inch, or it may be mixed with an appropriate amount of water to form a slurry which is subsequently passed through a spray dryer to form microspheres having a particle size of from 5 to 110 U.S. Standard mesh. In either case the particles formed are dried, preferably at a temperature of 200 to 300° F., and finally calcined at 700 to 1700° F., preferably 1000 to 1500° F. During the calcination aluminium chloride is removed from the particles by sublimation, providing the catalyst with the desired mechanical strength.

In one preferred procedure, the zeolite component is first mixed with an artificial matrix component to form a finely divided composite of zeolite in an inorganic matrix. Such compositions are commercially available and are sold as fluidized cracking catalyst having a particle size of from 5 to 110 U.S. Standard mesh. Such composites are then mixed with the clay component and the alumina sol to form the mixture which is shaped, dried and calcined.

Compositions obtained by the process of the invention find utility as hydrocarbon conversion catalysts; in particular those which contain rare earth metal ion-exchanged faujasite are very effective hydrocarbon cracking catalysts. The catalysts can also contain promoter metals such as cobalt, molybdenum, platinum, or other metals of Groups VI to VIII of the Periodic Table to form specialized hydrocarbon conversion catalysts, for example for use in hydrocracking, isomerization, hydrotreating and reforming processes.

The following Examples illustrate the invention.

#### Example I

An alumina sol was prepared by first mixing 82 kilograms of aluminium metal of particle size (diameter) 1/16 to 1/8 inch with 410 litres of aqueous hydrogen chloride solution containing 1.0 moles HCl per litre. The resulting mixture was then heated for about 9 hours at 200° F. During the reaction hydrogen was evolved and the solution became more viscous. Analysis of the solution finally obtained indicated that it contained 6.7% Cl and 24.9% alumina (calculated as  $\text{Al}_2\text{O}_3$ ) and that the  $\text{Al}(\text{OH})_3:\text{AlCl}_3$  molar ratio was 6.746.

#### Example II

A commercial cracking catalyst composite which contained 10% calcined rare earth metal ion-exchanged Type X zeolite, 40% kaolin clay and 50% artificial silica-alumina composite having an alumina content of 26%.

was milled and screened to a particle size range of 100 to 400 U.S. Standard mesh. 100 pounds of the catalyst composite was dry mixed with 37 pounds of kaolin clay for 20 minutes. Subsequently, 58 pounds of the alumina sol obtained in Example I was added, and the resulting mixture was milled to a plastic consistency for about 20 minutes and then extruded through a 5/32 inch die in a conventional extruder. The extrudates were tumbled for 40 minutes at a temperature of 80° F. and subsequently dried at 275° F. for 12 hours and calcined at 1200° F. for three hours. The resulting catalyst contained 5.5% zeolite, 51.5% clay and 33% artificial silica-alumina composite, all bound together by 10% alumina. This catalyst, as shown in Table I below, possessed considerably higher attrition resistance than a similar clay-containing catalyst which had been made using a conventional binder.

#### Example III

A catalyst was prepared from 63 pounds of kaolin clay identified as KCS clay, 63 pounds of Avery clay and 17 pounds of calcined rare earth metal ion-exchanged zeolite having a sodium content of 0.3% (calculated as Na<sub>2</sub>O). The components were dry mixed for 30 minutes and then mixed with 44 pounds of the alumina sol obtained in Example I. The resulting mixture was formed into beads having a size range of 4—10 U.S. Standard mesh in a conventional mixer. The beads were then rolled in a damp stage for 40 minutes and subsequently dried at 250° F. for 16 hours and

calcined at 1200° F. for 3 hours. The resulting catalyst contained 10% zeolite, 82% clay and 8% alumina (calculated as Al<sub>2</sub>O<sub>3</sub>).

#### Example IV

75 pounds of Avery clay, 75 pounds of KCS kaolin clay and 23 pounds of calcined rare earth metal ion-exchanged Type Y zeolite were dry mixed for 30 minutes and then combined with 80 pounds of the alumina sol obtained in Example I, after which mixing was continued for an additional 30 minutes. The product was transferred to a slurry tank to which 60 gallons of water and 40 grams of tetrasodium pyrophosphate were added to form a slurry having a solids content of 30%. This slurry was homogenized by passing it through a colloid mill and then spray dried at a temperature of 275 to 300° F. The microspheroidal particles obtained were then calcined at 1000° F. for three hours. The resulting catalyst contained 77% clay, 12.0% zeolite and 11% alumina.

#### Example V

To illustrate the outstanding mechanical strength and attrition resistance of the catalysts obtained in Examples II, III and IV, the attrition resistance of a sample of each was measured by the standard Accelerated Air Jet Attrition Test or the Davison Index Test. The same measurements were also made on control samples which contained about the same amount of clay and zeolite, but different binders, and also on two commercial catalysts. The results are shown in Tables 1 and 2.

TABLE I  
Bead Type Catalyst

% Sieve	Composition		Type of Binder	% Binder	% Attrition Loss by Accelerated Air Jet Attrition Test*			
	% Synthetic Matrix	% Clay			20 Min	1 Hr.	2 Hrs.	4 Hrs.
5.5	33	55.5	Polyvinyl Alcohol	3%	60	100	—	—
Catalyst of Example II			"Sterotex"	3%				
Catalyst of Example III					—	4.4	9.1	14
Commercial Bead Type Catalyst						5.3	11	15
					—	8.4	14.2	20.3
								25.5

\* A 30 gram sample previously screened on a U.S. Standard 10 mesh Screen is placed in an inverted one litre conical flask. The flask has a one-inch hole, covered by a 12 mesh screen, centred in its bottom. Dry air (Dew Point  $-40^{\circ}\text{F}.$ ) is admitted to the flask for a certain time at 6.1 standard cubic feet per minute. At the end of this time the material is rescreened on a 10 mesh screen and the material retained is weighed. The attrition loss is calculated as follows:

$$\% \text{ Attrition Loss} = \frac{(30 - x)}{30} \times 100, \text{ where } x \text{ is the weight of material in grams retained on the 10 mesh screen.}$$

12. A process according to Claim 10 or 11, wherein the mixture contains an artificial amorphous silica-alumina composite containing 10 to 30% by weight of alumina.
- 5 13. A process according to any one of the preceding claims, wherein the mixture contains also as a promoter a metal of Groups VI to VIII of the Periodic Table.
- 10 14. A process according to any one of the preceding claims, wherein the shaped composition is dried at a temperature of 200—300° F. and then calcined at a temperature of 700—1700° F.
15. A process according to Claim 14, wherein the dried shaped composition is calcined at a temperature of 1000—1500° F. 15
16. A process for the production of a catalyst according to Claim 1, substantially as hereinbefore described.
17. A catalyst obtained by a process claimed in any one of Claims 1 to 16. 20

J. A. KEMP & CO.,  
Chartered Patent Agents,  
14, South Square,  
Gray's Inn,  
London, WC1R 5EU.

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